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Title: Stable dye sensitized solar cells based on a gel electrolyte with ethyl cellulose as the gelator

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Abstract: A simple gelating process is developed for the conventional acetonitrile-based electrolyte of dye solar cells, based on ethyl cellulose as the gelator. The electrolyte becomes quasi-solid-state upon addition of an ethanolic solution of ethyl cellulose to the conventional acetonitrile-based liquid electrolyte. The photovoltaic conversion efficiency with the new gel electrolyte is only slightly lower than the liquid electrolyte; e.g. 6.5% for liquid electrolyte versus 5.9% for gel electrolyte with 5.8 wt% added ethyl cellulose. The ionic diffusion coefficient is not affected by the gelation, and the devices are remarkably stable for at least 550 h under irradiation at 55 °C. Realization of larger modules and panels using this gel electrolyte is investigated.

Dear Editor,

Hereby we submit a full paper with the following details:

**Title:** Stable dye sensitized solar cells based on a gel electrolyte with ethyl cellulose as the gelator

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**Prime novelty statement:**

A major obstacle in commercializing dye solar cells is the stability, mainly due to the strict requirements of sealing the liquid electrolyte cell. While some complex routes for the gelation of the electrolyte have been reported, we developed a facile route using ethyl cellulose as the gelator, which exhibits excellent stability of the cell parameters under working conditions (simulated sun light, 55 °C). The electrolyte is being used in our large demonstration dye solar panel (Sharif Solar).

**This manuscript and all its contents have not been published previously. In addition, it is not under consideration for publication elsewhere. The article is original, has been written by the stated authors who are all aware of its content and approve its submission.**

Sincerely yours,

Fariba Tajabadi,

Assistance Professor

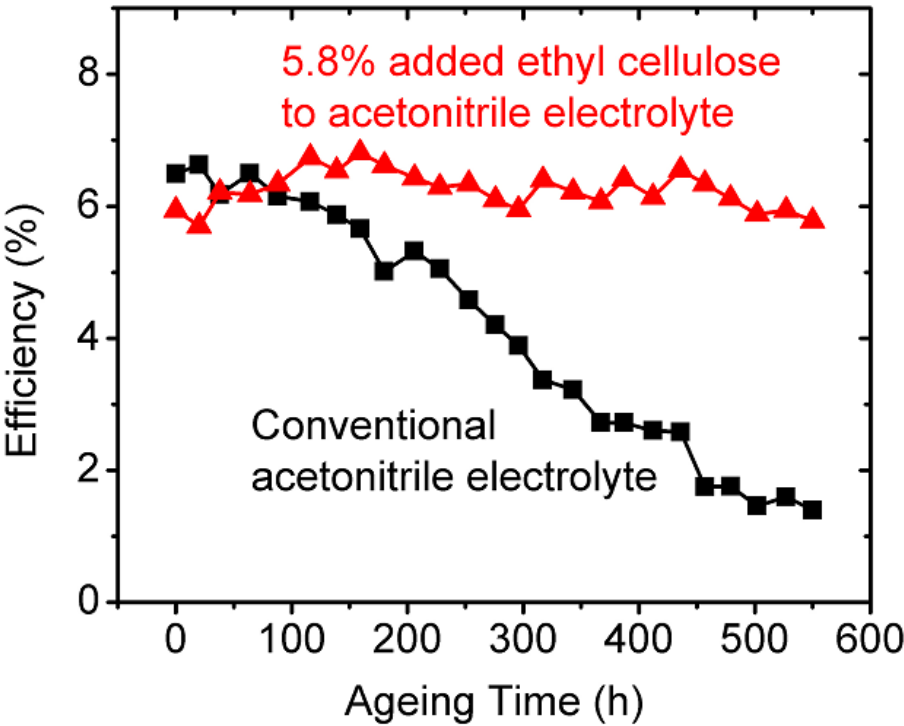
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**Research highlights**

- Ethyl cellulose was used as a gelator for the gelation of liquid electrolyte in dye sensitized solar cell.
- Gelation makes no remarkable change in ionic diffusion coefficient.

Resulting dye sensitized solar cells with gel electrolyte shows excellent stability under simulated sun light at 55 °C.

## Stable dye sensitized solar cells based on a gel electrolyte with ethyl cellulose as the gelator

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**Abstract:** A simple gelating process is developed for the conventional acetonitrile-based electrolyte of dye solar cells, based on ethyl cellulose as the gelator. The electrolyte becomes quasi-solid-state upon addition of an ethanolic solution of ethyl cellulose to the conventional acetonitrile-based liquid electrolyte. The photovoltaic conversion efficiency with the new gel electrolyte is only slightly lower than the liquid electrolyte; e.g. 6.5% for liquid electrolyte versus 5.9% for gel electrolyte with 5.8 wt% added ethyl cellulose. The ionic diffusion coefficient is not affected by the gelation, and the devices are remarkably stable for at least 550 h under irradiation at 55 °C. Realization of larger modules and panels using this gel electrolyte is investigated.

**Keywords:** Dye sensitized solar cell, quasi solid state, gel electrolyte, ethyl cellulose.

## 1 . Introduction

Dye-sensitized solar cells (DSSCs) have attracted extensive scientific and technological interest as a low cost and high-efficiency alternative to conventional inorganic photovoltaic devices (O'Regan and Gratzel, **1991**, Gratzel; *Nature*. **2001**). Although, efficiency over 11% has been recorded for DSSCs with volatile organic liquid electrolytes (Yella et al., **2011** ; Gratzel et al., **2004** ; Gratzel et al., **2005**; Chiba et al., **2006** ) there is a challenge for outdoor applications in view of the need for robust encapsulation. In order to be commercially viable, cells must be stable over a long period of time. However, various practical problems such as the leakage of the liquid electrolyte remain as serious barriers to their application. <sup>[4]</sup> For this reason; extensive efforts have been made to develop solid state DSSCs, which require no hermetic sealing. Two different types of solidification strategy exist. First is all-solid-state DSSCs having no solvent and based on hole transport inorganic or polymer semiconductors ( O'Regan and Schwartz **1996**; Tennakone et al., **2000**; Kim et al., **2004**; Yum et al., **2008**) . However, this type of DSSCs suffers from poor pore filling and fast recombination, resulting in relatively low efficiencies. Besides, hole conducting polymers have typically low hole mobility, that puts restriction on the polymer thickness. Recently, solid state DSSCs based on perovskite hole conductors such as CsSnI<sub>3</sub> have shown high efficiency close to liquid electrolyte DSSCs, but they are very sensitive to air moisture (Chung et al., **2012**). The second approach for improving DSSC stability is gelation of liquid electrolyte by addition a gelator or different nanostructures into the liquid electrolyte or replacing the volatile solvent by a less volatile solvent such as ionic liquids.

Different materials have been used for electrolyte gelation. Polymers, such as poly(ethylene glycol), (Kim, et al. 2004) poly(methyl methacrylate),( Li et al. , **2007**) poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP),(Wang et al., **2003** and Cui, **2013**) polystyrene, ( Lee et al., **2012** ) polyacrylonitrile, ( Chen et al., **2013**) and polyethylene oxide ( Shi et al., **2009**) have been used as additives for the solidification of liquid electrolytes. Among these polymers, PVDF-HFP results in high performance, highly stable cells in light soaking tests. As an alternative method, nanoclay, (Katakabe et al., **2007**; Wang et al., **2013**) SiO<sub>2</sub>, ( Wang et al., **2003**; Chen et al., **2014** ; Han et al., **2013**) <sup>[20- 22]</sup> and carbon nanotube (Zhanga et al., **2012**) have been applied for electrolyte gelation. Generally, dye solar cells with gel electrolytes suffer from lower efficiency compared with liquid electrolytes. There are reports that the additives can make gel electrolytes as efficient as liquid electrolytes, however, they need

additional synthesis process ( Lee et al., **2012** ; Wang et al., **2013**; Wang et al., **2003**; Chen et al., **2014**; Han et al., **2013**; Lun Chen et al.; **2013**; Nejati, et al., 2011; Li et al., **2014**)

Here, in this report we present a new and facile gelation method for the liquid electrolyte, which is based on ethyl cellulose (EC) polymer. Non-aqueous EC gel has been widely reported for application in drug delivery systems because of its ability to form a structured gel network, which demonstrates satisfactory rheological and mechanical properties (Chan et al., **2006**; Brunoa et al., **2012**). Ethanolic EC gel is usually used as a viscosity agent in TiO<sub>2</sub> paste fabrication. Recently, EC with carbon nanotube was used for electrolyte gelating in DSSC with long term stability (Yong and Jianyong, **2013**). However, it only forms gel at large EC concentrations, namely above 10%. Multi wall carbon nanotube at 1.5% wt is needed for electrolyte gelation in lower EC concentration. In this work we used ethanolic EC gel as a simple gelator for gelation of liquid electrolyte. The final solar cell with new gel electrolyte shows high stability and identical efficiency comparable with the liquid electrolyte. Also the developed electrolyte was employed to make larger cells with surface area of 100 cm<sup>2</sup>.

## **2. Experimental Section**

### **2.1. Gel Electrolyte preparation**

Liquid electrolyte composition contains 0.1 M LiI (Merck), 0.1 M I<sub>2</sub> (Merck), 0.5 M 4-tertbutylpyridine (Aldrich) and 0.5 M tetrabutylammonium iodide (Merck) in acetonitrile solvent. For gel electrolyte preparation, first a highly viscose solution of EC in ethanol is prepared by adding equal weights of two kinds of pure EC powders, i.e., EC (5–15 mPas, #46070, Fluka) and EC (30–50 mPas, #46080, Fluka), to yield 17.6 wt. % solutions. Then different amounts of EC ethanolic solution were added to the liquid electrolyte to get various EC electrolyte gels of 3.5 wt. %, 5.8 wt. % and 8.8 wt. %.

### **2.2. Solar cell fabrication**

TiO<sub>2</sub> photo-electrodes for DSSCs were coated by Doctor Blade deposition of a transparent nanocrystalline TiO<sub>2</sub> film of 8 μm thickness, consisting of ~20 nm TiO<sub>2</sub> nanocrystals and 4 μm scattering film. The pasted films were heat treated at 490 °C for calcination and sintering, and TiCl<sub>4</sub> treated in a solution of 40 mM for 30 min. The mesoporous films were dye loaded in a 0.3 mM N719 (B2, Dyesol) dye solution. Counter electrodes were prepared by thermal deposition of

0.3 mM  $\text{H}_2\text{PtCl}_6$  solution in ethanol, spread on FTO. 30  $\mu\text{m}$  Surlyn (Dyesol) spacers were used to seal the cells. The cells were filled with different electrolyte composition.

### 2.3. Characterizations

Electrolyte viscosity measurements were carried out using a Stabinger viscometer (SVM3000, Anton Paar). The J-V characteristics of the cells having an active area of  $0.28\text{ cm}^2$  were measured under AM 1.5 ( $100\text{ mWcm}^{-2}$ ) illumination using a solar simulator (Sharif Solar) coupled with a potentiostat (Palmsens) for recording the J-V plots. Electrochemical impedance spectroscopy tests were carried out using a potentiostat/ galvanostat (IVIUM, Compactstat) by a Pt-Pt cell. The stability tests were performed in a constant temperature box, kept at  $55\text{ }^\circ\text{C}$ , and the cells were constantly irradiated with high power white LEDs, with the light intensity adjusted so that the cells produce the same short circuit current as AM1.5.

## 3. Results and discussion

### 3.1 Gel rheology

As mentioned earlier, EC is the most widely used viscosity agent for the preparation of  $\text{TiO}_2$  pastes. EC forms a gel with high viscosity after dissolution in ethanol. However, ethyl cellulose fails to form any gel after room temperature dissolution in acetonitrile, which is the common solvent in liquid DSSCs. However, a viscose electrolyte forms by adding different amounts of the EC-ethanol gel to the liquid electrolyte based on acetonitrile solvent. Fig. 1 shows the viscosity variations of acetonitrile with different weight percents of EC, prepared by adding EC-ethanol gels to acetonitrile. Adding EC remarkably increases the viscosity of the gel. The viscosity for the 8.7% EC gel exceeds  $100\text{ mPa.s}$ , which is about 120 times higher than liquid electrolyte. The viscosity is also highly dependent on temperature; *i.e.* about 3 times lower when the temperature is raised from  $25\text{ }^\circ\text{C}$  to  $50\text{ }^\circ\text{C}$ . This property helps in easy penetration of electrolyte in  $\text{TiO}_2$  mesoporous structure and better cell filling, with a small increase in the temperature during the electrolyte filling. It has been reported that the mesoporous structure makes it especially difficult to be filled with these gel-type materials due to the viscous and steric effect (Nejati and Lau, 2011).

### 3.2 DSSC performance



Fig. 2 shows the current-voltage curves of different cells prepared with liquid electrolyte and gel electrolytes with different EC weight percent. The current density ( $J_{sc}$ ), open circuit voltage ( $V_{oc}$ ), fill factor ( $FF$ ) and efficiency ( $\eta$ ) are cited in Table 1. It can be seen that for EC contents from 3.5% to 8.7%, the loss in the photovoltaic performance of the cell is negligible (about 13%), while there is a remarkable increase in the viscosity of the gel electrolyte. For the liquid electrolyte,  $J_{sc}$ ,  $V_{oc}$ , and  $FF$  are  $17.0 \text{ mA cm}^{-2}$ , 0.67 V, and 0.52, respectively, yielding an overall conversion efficiency ( $\eta$ ) of 6.5%. There is a loss in cell efficiency with adding EC to the liquid electrolyte. The cell with the highest viscosity electrolyte exhibits  $J_{sc}$  value of  $14.2 \text{ mA cm}^{-2}$ ,  $V_{oc}$  value of 0.68 V, and  $FF$  value of 0.57, reaching an efficiency of 5.6%. The reduction of efficiency with an increase in the electrolyte viscosity is a known effect; and is due to the loss in ionic diffusion coefficient.

### 3.3 Electrochemical behavior

To quantify the diffusion coefficient of  $\text{I}_3^-$  ions in the gel electrolytes, EIS analysis was employed. Fig. 3 demonstrates Nyquist plots of various Pt-Pt cells using electrolytes with different EC contents. In general, the Nyquist plot of a Pt-electrolyte-Pt device shows two semi-circles in the frequency range 10 Hz to 100 KHz; one corresponding to the charge transfer resistance at the Pt-electrolyte interface (higher frequencies), and the other representing the Warburg diffusion process ( $R_{diff}$ ) of  $\text{I}_3^-$  in the electrolyte (lower frequencies). An equivalent circuit (Fabregat-Santiago et al., 2007) (Fig. 3) was used to model the data and calculate the diffusion coefficients of  $\text{I}_3^-$  ions in the electrolyte, as listed in the table on top of the figure. Despite the large increase in viscosity (about 300 times for 8.7% EC), there is a small decrease in the diffusion coefficient for the gel electrolytes. This explains the negligible loss of photovoltaic performance for gel electrolytes compared to the liquid electrolyte. Recently, similar behavior has been reported for nano clay and polymer gel electrolytes, yielding efficiencies close to liquid electrolytes (Lee., 2012, Wang., 2013, Changa., 2013). This suggests that the gel viscosity makes no major influence on the ionic transport in the electrolyte. It has been proposed that in gel electrolytes, besides the physical diffusion (in most liquid systems), another type of charge transport mechanism named Grotthus type or exchange-reaction process  $\Gamma + \text{I}_3^- \rightarrow \text{I}_3^- + \Gamma$  may also assist the current flow. In such cases, rapid charge transfer is enabled even in a viscous

medium, as physical transfer of species is not necessary for charge transport( Kawano., 2003; Rowley, 2010; Kim., 2012) .

### 3.4 Stability behavior

To investigate the long-term stability of the DSSCs with the new gel electrolytes, light soaking–aging tests were carried out on the sealed DSSCs. The cells were kept under irradiation equivalent to 1 sun at 55 °C, and their photovoltaic performance was recorded every day. Fig. 4 shows  $J_{sc}$ ,  $V_{oc}$ , FF and  $\eta$  in the course of time, for the liquid DSSC and the gel DSSCs with different EC content. It is clear that incorporating EC into the DSSC electrolyte makes remarkable enhancement in device stability. The  $V_{oc}$  of DSSCs with the liquid electrolyte and the gel electrolytes remains almost unchanged. For FF, gel DSSCs show minor variations over time, while the liquid DSSC starts to drop after about 350 h.  $J_{sc}$  decreases quickly and continuously for the liquid electrolyte cell, however, for the gel electrolytes no sign of drop in current density is observed. The efficiency is, consequently, well stable for the gel DSSCs.

Table 2 shows the photovoltaic parameters for the liquid and gel DSSCs after 550 h of light soaking. The efficiency of the device with the liquid electrolyte reaches 1.42%, which shows 78% loss compared to the initial value. However, the gel electrolytes with 5.8% and 8.7% EC in the electrolyte show stable conversion efficiency without any considerable loss. This demonstrates the low vapor pressure of the gels.

### 3.5 Realization of solar modules

The developed electrolyte was employed to make larger cells with improved stability. 10 cm × 10 cm modules were fabricated using a W-sandwich scheme as illustrated in Fig. 5a. The structure consists of 12 ribbon cells with 5.9 mm and 7.0 mm widths. The narrower cells are front-illuminated cells where the photoanode ( $TiO_2$ ) lies in the illumination side, and wider cells are back-illuminated cells. The widths of the cells were decided to attain current matching between the series cells, and was estimated based on the front and back illumination  $J_{sc}$  values. The ribbon cells were isolated by Surlyne spacers, with a very small spacing of 1 mm. Series connection was created by appropriate laser etching of the FTO film, as shown in Fig. 5a. The electrodes were prepared by screen printing and the usual heat treatment processes. The modules

were sealed using a home-made hot-press system. The gel electrolyte with 5.8% EC content was inserted into the cells using a home-made injection apparatus.

A number of modules were fabricated, for which the best modules showed 4.2% power conversion efficiency. The current-voltage graph and the picture of a 10 cm  $\times$  10 cm module are shown in Fig. 5b and 5c. A short circuit current of 65 mA and open circuit voltage of 8.8 V is obtained using a single module. The low fill factor of 0.54 indicates non-ideal series and shunt resistance, which need to be more optimized in future. Realization of a panel based on 64 gel-electrolyte based modules was tried as displayed in Fig. 5d. The modules were all connected in parallel.

#### **4. Conclusion**

In summary, we have introduced EC as a simple gelating agent for DSSC electrolyte. Addition of EC results in considerably higher electrolyte viscosity, while this makes no considerable influence on the ionic diffusion. The initial efficiency of devices is slightly reduced with increasing the EC content; up to 14% reduction for 8.7% EC. This may imply an important contribution of Grotthus mechanism for ion transport. The cells remain remarkably stable with addition of EC, that is, the efficiency shows no decrease after 600 h irradiation at 55 °C. The effectiveness of the synthesized gel electrolyte in large module fabrication is realized.

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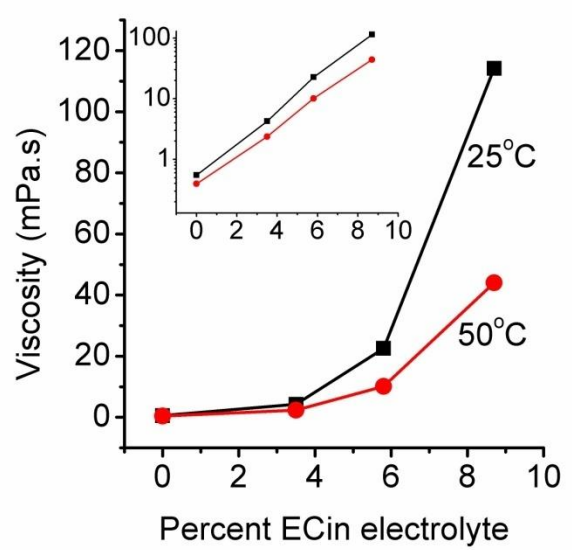


Fig. 1. Variation of acetonitrile viscosity with ethyl cellulose addition. The inset shows the semi-log plot. Viscosity values were measured at 25 °C and 50 °C.



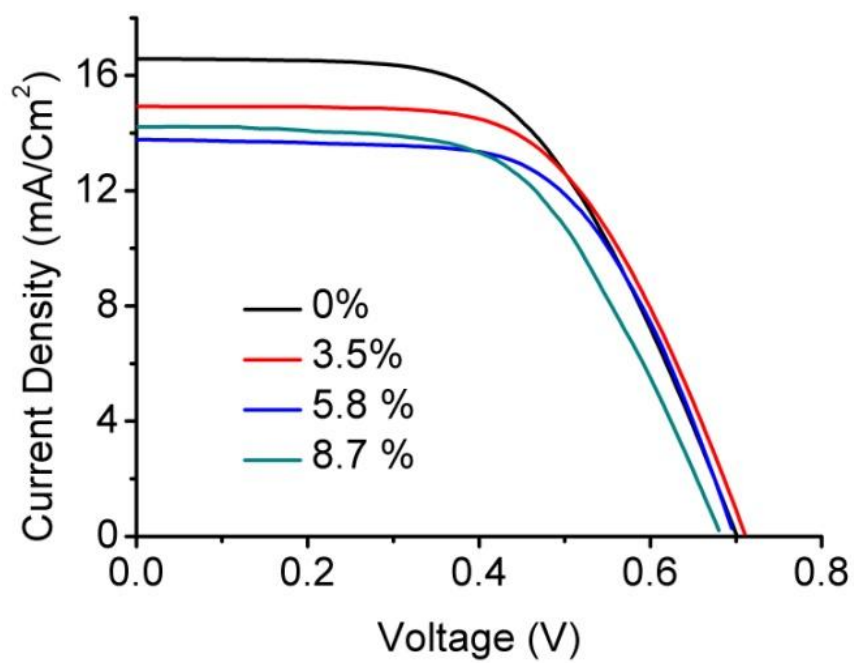


Fig. 2. J-V curves of DSSCs with electrolytes of different EC content.

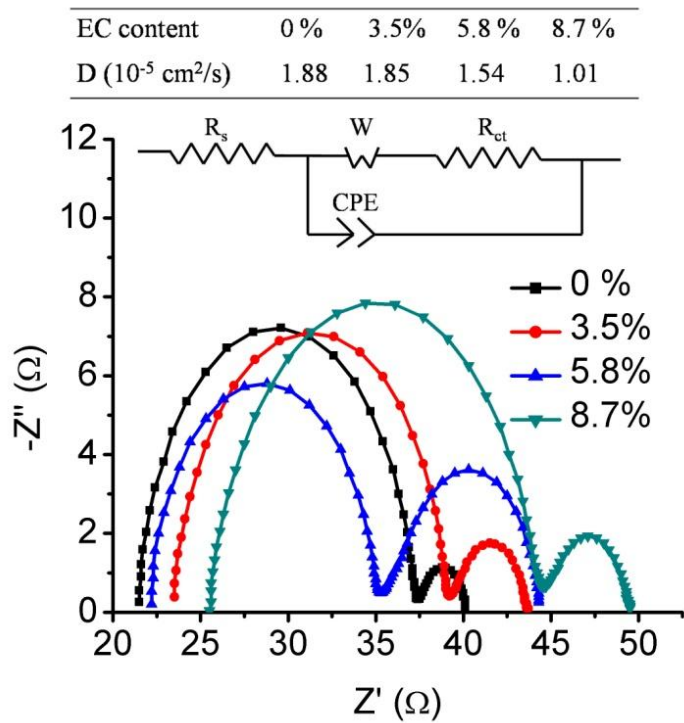


Fig. 3. The Nyquist spectra of the cells with liquid and gel electrolytes. The data is fitted using the shown circuit model to obtain the values of Warburg resistance, and consequently ionic diffusion coefficients. The estimated diffusion coefficients are listed in the table on top.

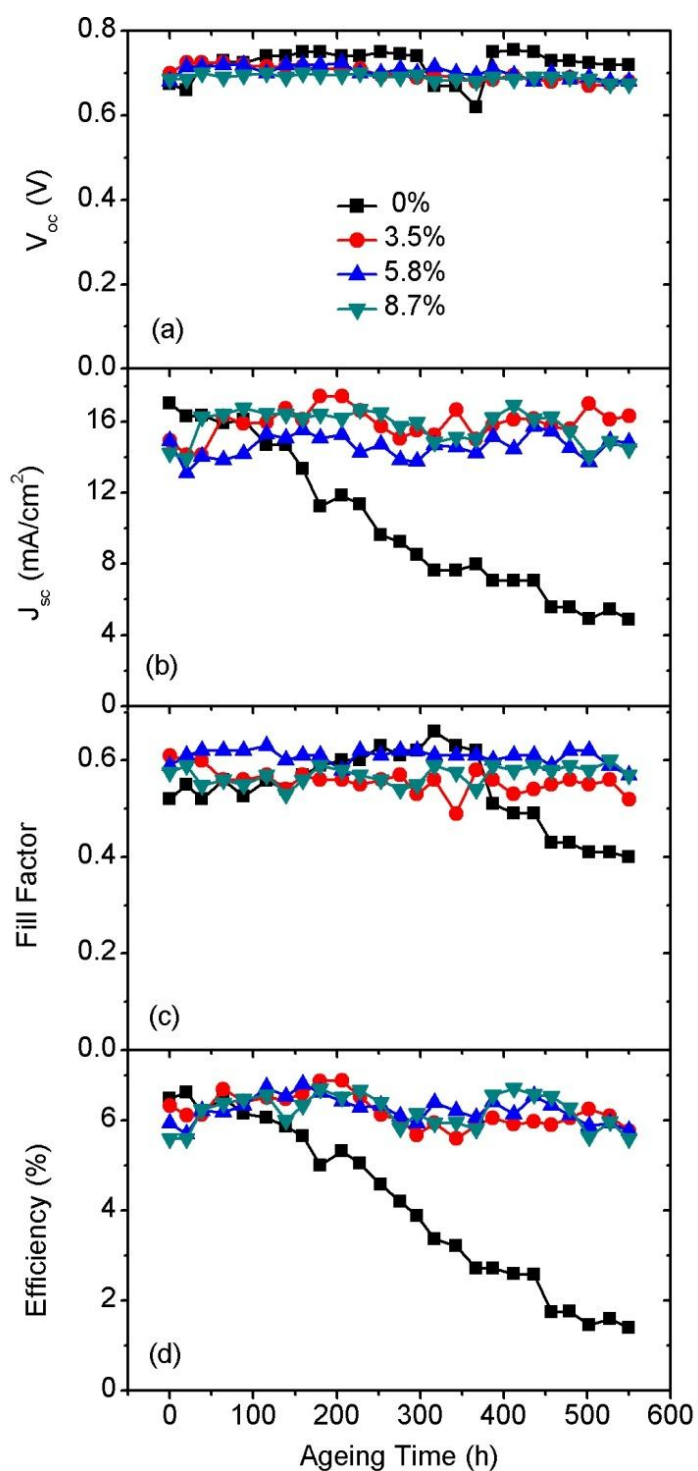


Fig. 4. Stability test data for the DSSCs with electrolytes of different EC content: (a) open circuit voltage, (b) short circuit current, (c) fill factor, and (d) efficiency. The tests were performed under 1 sun equivalent illumination and at 55°C.

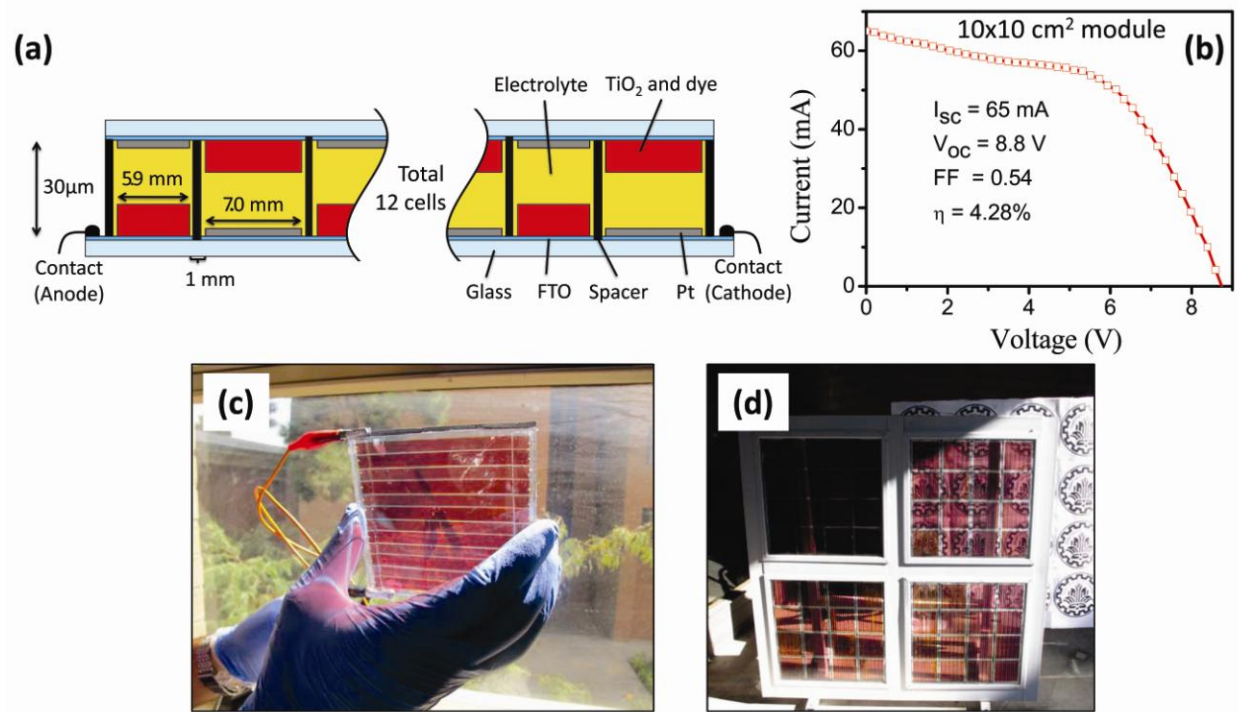


Fig. 5. (a) The schematic of the W-sandwich structure of the module consisting 12 ribbon cells in series. (b) Current-voltage graph of best modules measured under simulated sunlight. (c,d) The picture of the fabricated module and fabricated panel consisting of 64 modules in parallel.

Table 1  
Photovoltaic parameters of DSSCs fabricated with liquid and gel electrolytes with different EC content.

EC content	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$ (%)	$\eta$ (%)
0 %	0.67	17.0	52	6.5
3.5 %	0.70	14.9	61	6.3
5.8 %	0.68	14.9	59	5.9
8.7%	0.68	14.2	57	5.6

Table 2

Photovoltaic parameters of DSSCs with liquid and gel electrolytes after 550 h light soaking.

<b>EC content</b>	<b><math>V_{oc}</math> (V)</b>	<b><math>J_{sc}</math> (mA cm<sup>-2</sup>)</b>	<b><math>FF</math> (%)</b>	<b><math>\eta</math> (%)</b>	<b><math>\Delta\eta</math> (%)</b>
0 %	0.72	4.87	0.42	1.42	<b>-78.1</b>
3.5%	0.68	16.33	0.52	5.77	<b>-8.8</b>
5.8%	0.68	14.84	0.57	5.78	<b>-2.8</b>
8.7%	0.68	14.47	0.57	5.60	<b>0.0</b>